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A FEASIBILITY STUDY ON THE GROWTH OF BULK GAN SINGLE CRYSTALS.(U)
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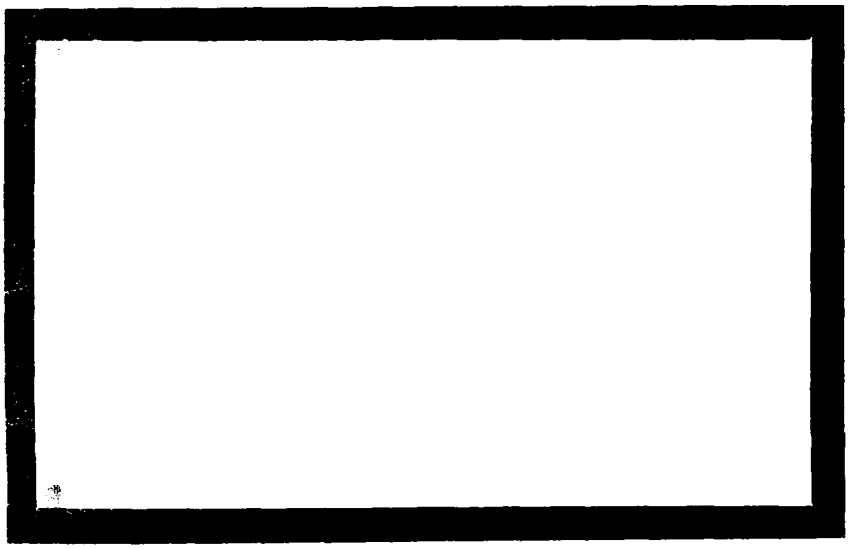

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Second Quarterly Report

on

A FEASIBILITY STUDY ON THE GROWTH OF BULK GaN SINGLE CRYSTALS

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INTRODUCTION

In the previous report, a breakthrough was reported in attempts to prepare large crystals of GaN, in that the maximum crystal size had been increased for the first time above 1 mm. The emphasis in the previous quarter has been to obtain an improved understanding of the factors leading to this improvement and so to determine the conditions necessary for the next advance. Experimental work has been concentrated on the horizontal crucible method which has shown the greatest promise to date.

EXPERIMENTAL RESULTS

A. Compartmented Growth Technique

In order to study in more detail the reaction between ammonia and liquid gallium, a series of experiments has been performed in which ten samples were located in separate recesses in a compartmented quartz crucible. The overall length of the crucible was 15 cm, as in the case of a single vitreous carbon boat, and the compartmented tube was located in the same temperature gradient as in previous experiments with the carbon boat (1010°-825°C). The ratio of ammonia to hydrogen flows was 2×10^{-3}, as in the experiments of Logan and Thurmond, and the hydrogen flow rate was about 225 cm^3/min. The reaction proceeded for 12 days in each case. Prior to crystal growth, the furnace was purged with hydrogen for 12 hours at room temperature, followed by 24 hours at about 1200°C.

In the first experiment, each compartment contained a drop of gallium weighing about 1.5 g. The aim of this experiment was to study the relative importance of surface and bulk reactions and to investigate the temperature dependence of the GaN formation reaction in the absence of convective flow along a continuous gallium sample.

It was found that at the hotter end of the crucible, the gallium drop had reacted almost completely to form GaN. The remaining gallium was in the form of fine inclusions trapped between GaN crystals. The resulting polycrystalline GaN product was in the form of a hollow dome, with rather larger crystals on the inside of the dome than on the outside. The initial reaction occurs at the Ga surface but this result is

evidence of short-range transport of dissolved GaN to the interior of the sample as the reaction proceeds. At temperatures below 1000°C, the GaN does not form a crust which prevents further reactions but sufficient space between crystallites must remain to allow the reaction to continue almost to completion over a period of several days.

At lower temperatures the GaN formation reaction is incomplete, and a relatively thin crust is formed during the period of the experiment. Simultaneously with the reaction to form GaN, there was loss of gallium which was strongly dependent on temperature. The sample at the hottest end was almost completely lost by evaporation or by reaction with an impurity (e.g., oxygen) in the gas stream. The evaporated gallium reacted with ammonia and was deposited as a coating inside the silica liner in the region at temperatures below about 900°C.

GaN whiskers were observed on samples which were at temperatures below about 950°C. The best crystals were formed by reaction at about 970° and 990°C, where crystals 0.6 to 1 mm in size were grown, the best-developed faces being at the edge of the gallium where it contacted the silica crucible. Even in the best samples, however, there was multiple nucleation and the larger crystals grew in competition with many smaller crystals. An example of growth from this experiment is shown in Fig. 1.

This experiment demonstrated that similar crystals could be obtained without a temperature gradient along a long sample of gallium (as in the Logan and Thurmond experiment). Although surface reaction between Ga and NH_3 is clearly dominant, there is evidence of bulk flow of dissolved GaN. A temperature of about 980°C appears optimum for crystal growth, but multinucleation remains a severe problem.

In the second experiment, polycrystalline seeds typically 4 mg in weight were inserted in each of the compartments, and the gallium contained in a silica boat located remotely at the hot end of the furnace. The same flow of $NH_3 + H_2$ was maintained over the gallium, the aim being to determine whether vapor transport by direct reaction of Ga with NH_3, or via oxygen impurities in the hydrogen, would give stable growth

Figure 1. Edge of sample, grown at 970°C (100X).

Figure 2. GaN polycrystalline seed showing new growth by a hillock mechanism at approximately 850°C (33X).

on the seeds. Vapor transport was found in several experiments to produce coatings of GaN on the silica liner of the furnace.

SEM photographs of the seeds after this experiment showed no significant growth. However, some crystals were covered with very fine needles of β-Ga_2O_3, as a result of an air leak which occurred over the last two days of the experiment. The main conclusion was, however, that GaN crystals normally grow by a mechanism involving liquid Ga rather than by a vapor process.

In the third experiment, Ga drops and polycrystalline seeds (with 5-10 crystals) were inserted together into the recesses in the same quartz crucible, and the experiment repeated. As in the first experiment, there was a net loss of weight of the first four samples (approximately 1010°-950°C) while samples in the cooler region all showed a weight gain. The first two samples (T>990°C) showed evidence of decomposition, presumably through the reaction

$$2GaN \rightarrow 2Ga + N_2\uparrow$$

The best-formed crystals were those grown in the range from about 970°C to 880°C; again the largest crystals grown were about 1 mm in largest dimension. Although in most cases the larger crystals nucleated and grew in competition with the seeds, sample #2 (approximately 850°C) apparently grew by the addition of growth hillocks, presumably at sites where screw dislocations intersected the surface (Fig. 2). The growth rate at this temperature is low, the crystal increasing in weight from 5.1 mg to 6.4 mg. This example demonstrates that secondary nucleation can be avoided but the morphology of the grown layer is not smooth at this temperature. The density of active dislocations is in the region of $10^4 cm^{-2}$.

In contrast the {0001} crystal surface shown in Fig. 3 is of good morphology, free from hillocks or secondary nuclei. Crystals grown above 970°C in this case showed an irregular surface due presumably to the decomposition reaction. An example is shown in Fig. 4.

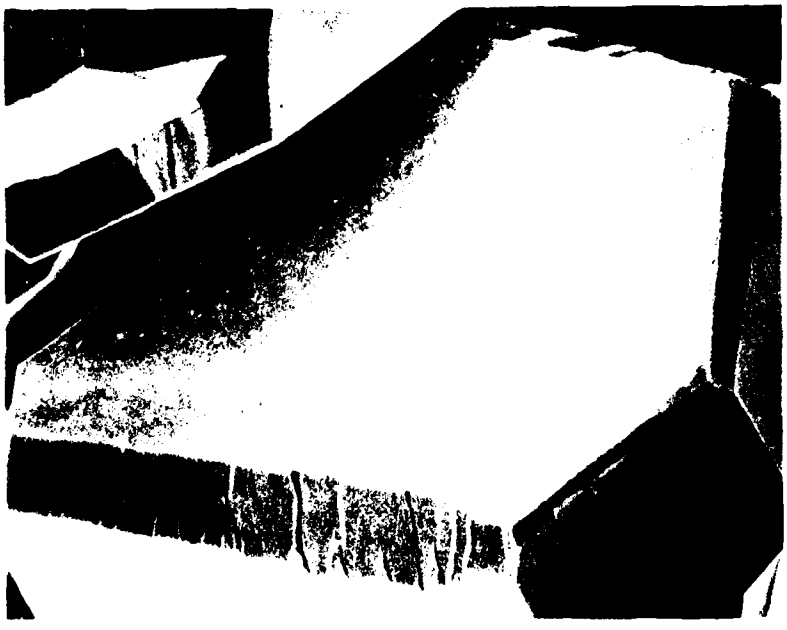

Figure 3. Smooth surface of crystal grown at approximately 945°C (1000X).

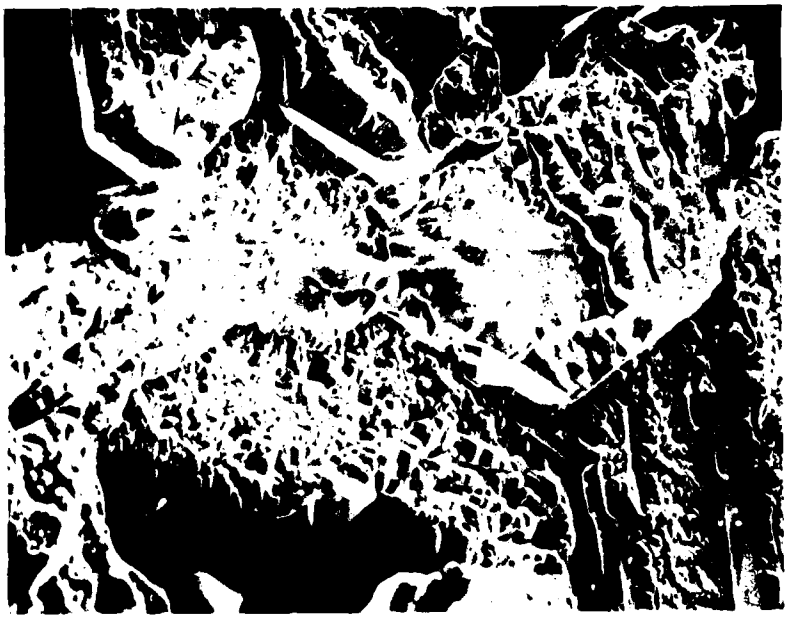

Figure 4. Surface of crystal cluster grown at 1010°C (210X).

B. Transparent Furnace

As an alternative means of studying growth and nucleation of GaN, a Transtemp gold-coated transparent furnace has been purchased and used initially to observe GaN crystallization in a long vitreous carbon boat as used for earlier studies. The maximum operating temperature of this furnace is limited, because of gold evaporation, to a value below 1000°C and so the temperature of the hot end of the boat has been set at 970°C. The temperature gradient is also lower, roughly one-fifth used in previous experiments, and the NH_3 partial pressure was about 1.4×10^{-3}. Three graphite wafers were placed on the top of the gallium in the first experiment using this furnace, the aim being to coat these with GaN for subsequent regrowth in a stirred, vertical crucible.

The gallium was observed to move about 1 inch from the hot end on raising the temperature to the steady value, so that one wafer fell to the bottom of the crucible. Nucleation of GaN began around the edge of the wafer at the colder end of the crucible, and the nucleation of small crystals subsequently occurred around the end of the liquid. Further nucleation was observed on the liquid surface ahead of the established nuclei, so that a discontinuous GaN film spread from the cold end and, to a lesser extent, from the walls. After a week, nucleation could also be detected on the central graphite wafer. Only after about 10 days did the crystals nucleated at the cool end begin to grow appreciably larger. The largest crystals grew at the hot end, around the graphite wafer and the edge of the melt.

C. Conductivity Measurement

The electrical conductivity of crystals about 1.5 mm long and 0.4 mm in diameter was measured by a two-contact method with an indium amalgam contact applied to each end. The measured conductivity along the c-axis was 1-5 $(\Omega cm)^{-1}$, the higher value being more reliable. Typical material grown by other investigators has $n \sim 10^{19} cm^{-3}$ and $\mu \sim 10\text{-}10^{2} cm^{2} V^{-1} s^{-1}$, so that $\sigma \sim 20\text{-}200\ (\Omega cm)^{-1}$. The low value of conductivity of our crystals may be due to a lower defect concentration, or to a low mobility, but the method of measurement may underestimate the true conductivity by an order of magnitude because of the contact resistance. Four-probe measurements are planned when larger crystals become available.

SUMMARY AND CONCLUSIONS

1. GaN crystals similar to those grown by the thermal gradient method of Logan and Thurmond can be produced from a compartmented crucible with each section containing a drop of gallium. The reaction proceeds almost to completion in 12 days at about 950°C.

2. The reaction proceeds by dissolution of active nitrogen, primarily as a surface reaction with bulk Ga or a surface film wetting GaN, but there is evidence of transport of GaN in solution over short distances. Chemical transport is unimportant except as a means of depositing GaN powder on the furnace lining.

3. The optimum temperature for GaN growth by direct reaction between NH_3 and gallium appears to be between 900° and 970°C.

4. Nucleation of GaN occurs readily in comparison with growth on established nuclei.

FUTURE PLANS

The low supersaturation for nucleation of GaN in comparison with that for crystal growth suggests that a lower vapor pressure of ammonia is necessary if multiple nucleation is to be avoided. With existing apparatus, it is not possible to achieve a stable flow below 0.4 cm^3/min. The supersaturation may, of course, be reduced by increasing the rate of flow of hydrogen carrier gas, but then the duration of experiments using a single tank is reduced. It is, therefore, planned to borrow or rent a Massflow meter to deliver a stable flow of ammonia at lower rates. Fluctuations in the gas flows are probably highly deleterious to the growth of large crystals, and improved stability is considered of great importance.

Plans are also in hand to purify the hydrogen carrier gas using a catalyst and cold trap. The catalytic unit was, in fact, introduced during the previous quarter but air leaks at the glass-metal joints prevented positive results.

Further attempts will be made to grow crystals in a stirred, vertical crucible by transport of previously synthesized material. This method offers the advantage that it is independent of the flow rate or purity of a gas stream.